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PROVISIONAL SPECIFICATION

Applicant(s):

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION

Invention Title:

SOLVENT EXTRACTION PROCESS FOR SEPARATING COBALT AND/OR MANGANESE FROM IMPURITIES IN LEACH SOLUTIONS

The invention is described in the following statement:

SOLVENT EXTRACTION PROCESS FOR SEPARATING COBALT AND/OR MANGANESE FROM IMPURITIES IN LEACH SOLUTIONS.

The present invention relates to a process for separating cobalt and/or manganese from calcium and magnesium contained in an aqueous solution such as an aqueous leach solution, and for recovering the cobalt and/or manganese where desired.

The world mineral industry is experiencing an unprecedented interest in metal extraction from laterite and sulphide ores through hydrometallurgical processes. Commonly, the hydrometallurgical process involves grinding, leaching and solvent extraction (SX), with recovery of product via precipitation or reduction processes. The intensity of the leaching process (temperature, pressure, bio) depends on the nature of the ore (mineralogy, grade), the distribution of the metal(s) to be recovered and the particle size reduction achieved during grinding. Leach solutions often contain copper, nickel, cobalt and zinc (and/or manganese) as metals to be recovered (target metals), with calcium, magnesium, iron and aluminium (and manganese if not be to be recovered) as impurity metals to be rejected. Iron (as ferric) and aluminium are often removed by precipitation at low pH (pH 2.5 - 5.0) prior to SX.

Separations of industrial significance that have proven to be particularly troublesome include:

- the separation of cobalt (and optionally nickel) from manganese (and calcium and magnesium), where manganese is to be rejected, and
- the separation of manganese (and cobalt and nickel) from calcium and magnesium, where manganese is to be recovered.

Traditionally, sulphide or hydroxide precipitation followed by re-leach processes have been used by industry to effect these separations.

Drawbacks of sulphide precipitation include:

- The separation of manganese from cobalt by sulphide precipitation is incomplete and causes problems in the downstream processes.
- The re-leaching of sulphides needs high temperature and pressure, indicating high capital and operating costs.
- The separation of copper and zinc from nickel and cobalt needs separate processes.

The drawbacks of the hydroxide precipitation process include:

- The use of magnesia as precipitation agent (if used to prevent gypsum formation) adds cost to the operation.
- Manganese is partially precipitated.
- The use of ammoniacal leaching (if used) to separate cobalt from manganese results in complexity of the flowsheet and causes serious problems in the downstream processes.
- Ammonia is expensive and the scrubbing and recovery of ammonia are difficult.
- The separation of copper and zinc from nickel and cobalt needs separate processes.

It is an object of the invention to provide alternative processes for:

- Separating cobalt from calcium and magnesium, and optionally manganese, especially for solutions deficient in nickel, and
- Separating manganese from calcium and magnesium, especially for solutions deficient in cobalt and nickel.

Summary of the Invention

The present invention is generally based on the development of an organic solution of a carboxylic acid and a hydroxyoxime which is effective in shifting the pH isotherms of nickel, cobalt, copper, zinc, magnesium, manganese and calcium in such a way as to enable separation of certain groups of these elements from each other. In particular, the isotherms of the elements copper, zinc, nickel and cobalt are separated from the isotherm of manganese to allow effective separation of manganese from these elements. Further, the isotherm of manganese is sufficiently separated from the isotherms of calcium and magnesium to allow effective separation of these elements from each other. Thus, when used in combination with certain leach solutions containing appropriate levels of elements, and in appropriate pH conditions, it becomes possible to separate (and optionally thereafter recover) cobalt and/or manganese from calcium and magnesium. Under some conditions, the organic solution of carboxylic acid and hydroxyoxime may be susceptible to degradation, particularly with respect to the hydroxyoxime component. Accordingly, a stabilizer may advantageously be added.

According to the present invention there is provided a process for the separation of cobalt and/or manganese from impurity elements selected from one or more of calcium and magnesium contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using an organic solution of a carboxylic acid and a hydroxyoxime. The organic solution may optionally further comprise a stabilizer.

The present invention is a particular example of a more general process for separating one or more of nickel, cobalt and manganese from the impurity elements calcium

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and magnesium contained in a leach solution, which process comprises the steps of subjecting the leach solution to solvent extraction using a carboxylic acid and a hydroxyoxime. The process of the invention that is the subject of this application is particularly suited to leach solutions containing low levels of nickel, since nickel has slow extraction and stripping kinetics in the absence of further additives.

The solvent extraction step described above achieves very good separation of cobalt (and/or manganese) present in the leach solution from (manganese,) calcium, magnesium and chloride impurity elements which may be present, and good separation of cobalt from manganese if cobalt is to be recovered and manganese is to be rejected as an impurity element. If zinc and copper are present, the process comprises separation of zinc, copper, cobalt and/or manganese from impurity elements selected from one or more of calcium and magnesium contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using an organic solution comprising a carboxylic acid and a hydroxyoxime. According to a preferred embodiment, the organic solution further comprises a stabilizer.

According to one embodiment, the elements cobalt and/or manganese extracted into the organic phase during solvent extraction are recovered therefrom. Where the organic phase of the extraction step contains primarily cobalt or manganese alone, the recovery step may comprise bulk stripping of the element from the organic phase. The bulk stripping may optionally be combined with ion exchange to remove any minor amounts of impurity elements, such as zinc, copper and nickel to improve the purity of the recovered elements. Another optional process for improving the purity of the recovered element is sulphide precipitation. Sulphide precipitation is more suited to

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precipitation of any minor amounts of copper, zinc, cobalt and nickel present in the manganese recovered from stripping.

In the situation where the leach solution contains both cobalt and manganese, the recovery step may comprise selective stripping of the organic phase to separate the manganese from the cobalt. The manganese may thereafter be recovered from the loaded strip liquor, and the cobalt recovered from the selectively stripped organic solution by bulk stripping.

Brief Description of the Drawings

The invention will be described in further detail with reference to the following figures which relate to preferred embodiments of the invention.

Figures 1 and 2 are graphs comparing extraction pH isotherms of metals using a comparative extraction system (Figure 1) and the extraction system of one embodiment of the invention (Figure 2).

Figure 3 is a graph showing the extraction kinetics of metals from a leach solution using the extraction system of one embodiment of the invention.

Figure 4 is a graph showing the stripping kinetics of metals from a loaded organic phase from the extraction system of one embodiment of the invention.

Figure 5 is a graph comparing stripping kinetics of cobalt using a comparative extraction system and the extraction system of one embodiment of the invention.

Figures 6 and 7 are graphs comparing extraction pH isotherms of metals using a comparative extraction system

(Figure 6) and the extraction system of one embodiment of the invention (Figure 7).

Figure 8 is a graph showing the extraction kinetics of manganese from a leach solution using the extraction system of one embodiment of the invention.

Figure 9 is a graph showing the stripping kinetics of manganese from a loaded organic phase from the extraction system of a one embodiment of the invention.

Figure 10 a schematic flow chart of the steps of the process of one embodiment of the invention.

Figure 11 is a schematic flow chart of the steps of the process of a second embodiment of the invention.

Figure 12 is a schematic flow chart of the steps of the process of a third embodiment of the invention.

Figure 13 is a schematic flow chart of the steps of the process of a fourth embodiment of the invention.

Detailed Description of the Invention

At the core of the present invention is a synergistic solvent extraction step which effects extraction of a large proportion of the nickel, cobalt, copper, and zinc into an organic phase (to the extent that these elements are present), with a large proportion of the calcium, magnesium, and chloride being rejected to the aqueous phase. Depending on the pH selected, the manganese can report to either the organic phase or the aqueous phase, as is chosen for a particular leach solution. The solvent extraction is conducted with a combination of carboxylic acid and a hydroxyoxime synergist, and optionally a stabilizer.

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The hydroxyoxime synergist is capable of increasing the pH gap, ΔpH_{50}, between isotherms for nickel and cobalt and that for manganese, and between the isotherm for manganese and those for calcium and magnesium. This results in advantageous selectivity of nickel and cobalt and optionally manganese, over the impurities (manganese), calcium, magnesium and chloride.

The pH_{50} value is the pH at which 50% metal extraction is achieved. Thus, ΔpH_{50} is the difference between the pH_{50} values for two metals, or the difference between the pH_{50} values for the same metal under different extraction conditions.

Carboxylic acid

In the most preferred embodiment of the invention, the carboxylic acid is 2-methyl, 2-ethyl heptanoicic acid (commercially available as Versatic 10) or a cationic exchange extractant having extraction characteristics similar to 2-methyl, 2-ethyl heptanoic acid could be used. Cationic exchange extractants have hydrogen ions which are exchanged with metal ions in the aqueous solution. The term carboxylic acid is used in its broadest sense to refer to any organic carboxylic acid. Carboxylic acids have the formula RCOOH, in which R represents any optionally substituted aliphatic or aromatic group, or combinations of these groups, including optionally substituted alkyl, alkenyl, alkynyl, aryl, or heteroaryl groups (and combinations thereof). Preferably R represents a relatively bulky group containing at least 4 carbon atoms, and preferably between 4 to 18 carbon atoms.

The term "alkyl" used either alone or in a compound word such as "optionally substituted alkyl" or "optionally substituted cycloalkyl" denotes straight chain branched or mono- or poly-cyclic alkyl, preferably C1-30 alkyl or

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cycloalkyl, most preferably C4-18 alkyl. Examples of straight chain and branched alkyl include methyl, ethyl, butyl, isobutyl, tert-butyl, 1,2-dimethylpropyl, 1-methylpentyl, 5-methylhexyl, 4,4-dimethylpentyl 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,1,2-trimethylbutyl, nonyl, 1- 2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 2-hexyl 2-methyloctyl and the like. Examples of cyclic alkyl include cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl and cyclodecyl and the like. The alkyl may optionally be substituted by any non-deleterious substituent.

In this specification "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthiom benzylthio, acylthio and the like.

Suitable optional substituents will be chosen on the basis that the carboxylic acid have the desired extraction characteristics, and the substituents do not react with any other component of the mixture under the given extraction conditions.

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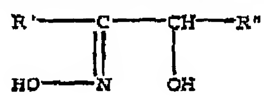
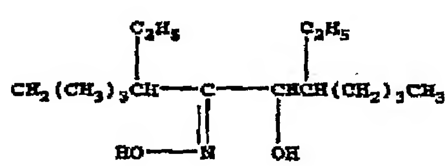
Hydroxyoxime

A hydroxyoxime is used as a synergist with the carboxylic acid in the solvent extraction step. A hydroxyoxime is a compound containing an oxime group and a hydroxy group. Preferably, the groups are in an α-position with respect to each other. Such α-hydroxyoximes are chelating, whereas oximes are generally non-chelating and thus behave differently. The "oxime" functional group contains a carbon to nitrogen double bond, with the nitrogen atom being attached to an oxygen atom. Accordingly, the term oxime includes within its scope oximes with a hydroxy group attached to the nitrogen atom, and oxime ethers, although hydroxime (>C=N-OH) is preferred. The hydroxyoxime may be a C8-C26 hydroxyoxime. Preferably, the hydroxyoxime is an aliphatic hydroxyoxime. Preferably, the hydroxyoxime is of the formula:



in which R' and R" are each selected from an optionally substituted, straight chain, branched or cyclic alkyl, group containing from 2 to 12 carbon atoms. Preferably each of R' and R" are unsubstituted alkyl groups, most preferably a heptyl group. An example of such a compound is 5,8-diethyl-7-hydroxy-6-dodecanone oxime (the active component of a commercial agent LIX 63). This has the following structure:



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Stabilizer

Under some conditions, the reagent mixture of carboxylic acid and hydroxyoxime may be susceptible to degradation, particularly with respect to the hydroxyoxime component. Accordingly, a suitable stabilizer may advantageously be used to slow any degradation reaction. Degradation may take place via a number of mechanisms, including oxidation and hydrolysis. Hence the stabilizer is suitably one that mitigates against oxidation and/or hydrolysis of the hydroxyoxime. Such stabilsers include, but are not limited to, esters (e.g. TXIB), ethers, ketones, alcohols (e.g. isodecanol, TDA) and alkylphenols (e.g. nonylphenol, dodecylphenol, BHT, Ionol). Preferably the stabilizer is an anti-oxidant. Of these, we have found the alkylphenol anti-oxidants to be particular useful. The term "alkylphenol" encompasses all alkyl derivatives of phenol, and in particular those derivatives with one or more straight chain, branched or cyclic alkyl substituents. The alkylphenol 2,6-bis(1,1-dimethylethyl)-4-methyl phenol (commercially available as BHT and Ionol) or reagents with similar anti-oxidant characteristics to 2,6-bis(1,1-dimethylethyl)-4-methyl phenol are particularly useful.

Leach solution

The leach solution subjected to the synergistic solvent extraction with the organic solution of carboxylic acid, hydroxyoxime and optionally a stabilizer may be any type of leach solution containing cobalt and/or manganese, together with impurity elements selected from one or more of calcium, magnesium, (manganese) and chloride, optionally together with copper and zinc. Preferably, the leach solution is one containing little nickel.

In this respect, the leach solution suitably contains less than 100ppm nickel, or any other low level that does not warrant recovery for economic reasons. Where cobalt is to

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be recovered, the nickel is suitably present in any amount of less than 50% of that of cobalt (for example, <100ppm nickel, >200ppm cobalt).

According to one embodiment, the leach solution may contain the following levels of elements:

Ni: 0 - 100 ppm
Co: 100 ppm - 5 g/L
Cu: 0 - 100 ppm
Zn: 0.2 - 2 g/L
Ca: saturated (0.5 - 0.7 g/L)
Mn: 1 - 50 g/L
Mg: 2 - 100 g/L

The leach solution may for instance be a pregnant leach solution obtained from the pressure acid leaching of any suitable ore type, such as a laterite or sulphide ore. It may alternatively be a solution from bio-leach, atmospheric acid leach, oxidative leach, reductive leach, chloride leach or any combination of these leach processes. The steps involved in producing such leach solutions are well known in the art.

The leach solution is preferably a solution that has been subjected to a preliminary iron and/or aluminium precipitation step to precipitate out iron and/or aluminium to leave an aqueous leach solution containing the target elements and impurity elements identified above. The leach solution may alternatively or further have been subjected to one or more additional treatment or processing stages.

<u>Synergistic solvent extraction conditions</u>

The solvent extraction step involves contacting an organic solvent containing the carboxylic acid, hydroxyoxime and optionally stabilizer with the (aqueous) leach solution.

The organic solvent may be any suitable organic solvent known in the art. Kerosene is the most common solvent/diluent used for this purpose due to its low cost and availability. Shellsol 2046 is one specific example.

The amount of carboxylic acid and hydroxyoxime (and stabilizer) in the organic solution used in the solvent extraction step will depend on the concentration of the (nickel), cobalt (and optionally manganese) or both to be extracted and the A/O (aqueous/organic) flow rate ratio. The concentration would typically be in the range of from 0.1 to 2.0 M for carboxylic acid, with a preferred range of 0.1 to 1.0M, and 0.05 to 1.0 M for hydroxyoxime. The concentration of stabilizer may be in the range of from 0 to 0.1 M, typically 0.005 to 0.1 M.

Preferably, the pH of the aqueous phase is maintained in a range from 3.5 to 5.0 and more preferably 4.0 to 4.5 in the extraction step if manganese is to be rejected. Preferably, the pH of the aqueous phase is maintained in a range from 5.5 to 7.0 and more preferably 5.8 to 6.3 in the extraction step if manganese is to be recovered. The temperature is preferably maintained in the range of from 10°C to 60°C, more preferably from 20 to 40°C. Whilst temperatures as low as 10°C are achievable, a temperature lower than 15°C results in high viscosity. At temperatures higher than 60°C there is a risk of evaporation and degradation of the organic phase.

The aqueous to organic ratio (A/O) in the extraction step is most suitably 1:1, but may lie in the range from 10:1 to 1:10, and preferably 1:5 to 5:1. The aqueous to organic ratio maintained in the scrubbing step may lie within the range from 1:5 to 1:200, but preferably it is in the range of 1:5 to 1:20.

The cobalt and/or manganese extracted into the loaded

organic phase in the synergistic solvent extraction can be recovered in downstream processing stages.

Scrubbing

The organic phase from the synergistic extraction step of the invention is suitably subjected to scrubbing. The scrub solution may suitably be a process stream recycled from the process, and is preferably derived from an aqueous stream of a stripping stage (which may be a selective stripping stage) following the scrubbing stage.

Recovery of cobalt, manganese or both from scrubbed organic solution

There are a number of options envisaged by the applicants for the recovery of cobalt, manganese or both from the scrubbed organic solution. One example for the situation where both cobalt and manganese are extracted (i.e. pH of aqueous phase in extraction is 5.5 to 7.0) is set out below. It is noted that other options within the skill and knowledge of those in the art could be used in place of the following, and are within the scope of the present invention. Moreover, different steps would be used for different leach solutions containing different levels of elements, or when other elements are desired to be recovered or removed.

Selective stripping to separate cobalt and manganese

According to one embodiment of the invention, the organic phase containing cobalt and manganese is subjected to selective stripping to separate to a significant extent the cobalt and the manganese. The selective strip suitably involves contacting the organic phase from the synergistic extraction with an acidic aqueous solution to yield (a) a loaded strip liquor containing manganese and (b) a selectively stripped organic solution containing cobalt (and zinc, nickel and copper, if they were present in the organic phase from the synergistic extraction).

The acidic aqueous solution for the selective strip is suitably sulphuric acid solution, although other aqueous acid solutions known in the art (such as hydrochloric) may be used. The pH of the acidic aqueous solution is suitably in the range of about 4.0 to 5.0, depending on the level of separation desired. Most preferably, the pH is about 4.5.

The combination of the described synergistic extraction with the selective strip of manganese from cobalt is a very useful combination, enabling the recovery of manganese and cobalt using only one solvent extraction circuit (although more than one circuit could be used if so desired with other process steps).

Other process details

The synergistic extraction step of the present invention may be combined with different preliminary and following process steps for the development of process suitable for the recovery of cobalt and/or nickel when different impurity elements may be present.

It will be well understood to persons skilled in the art of the invention that scrubbing stages of the type well known in the art may be used for recovering elements even if the scrubbing stages are not specifically mentioned. The design of the optimum arrangement of scrubbing stages will depend on the specific aqueous leach solution and the elements desired to be recovered therefrom (and target percentage recovery levels).

It is also an advantage of the present invention that cobalt can be separated from impurities contained in leach solutions without intermediate precipitation of the cobalt with other impurity elements and re-leaching of the

precipitate to subsequently enable the removal of the impurities. Thus, in a preferred embodiment of the invention, the process does not include a precipitation step involving precipitation out of the target elements and re-leaching of the precipitate.

Examples

The present invention will now be described in further detail with reference to the following examples which demonstrate the underlying theory behind the invention, and how the invention is put into practice.

Batch Test Work

Example 1 - Extraction pH isotherms of metals with Versatic 10 / LIX63 synergistic system.

This example illustrates that when carboxylic acid Versatic 10 is used as the extractant with no added synergist, the pH isotherms of the "valuable" elements Zn, Ni, and Co are too close to the isotherms of the "impurity" elements Mn, Ca and Mg for effective separation. However when a synergistic system comprising Versatic 10 and hydoxyoxime LIX 63 is used, the isotherms of the "valuable" elements Cu, Zn, Ni, and Co are sufficiently separated from the isotherm of Mn to allow effective separation. Further, the isotherm of Mn is sufficiently separated from the isotherms of Ca and Mg to allow effective separation.

The aqueous solution was a synthetic solution to simulate a typical laterite leach solution containing 3 g/L Ni, 0.3 g/L Co, 0.2 g/L Cu and Zn, 2 g/L Mn, 10 g/L Mg and 0.5 g/L Ca.

The metal extraction pH isotherms with the 0.5 M Versatic 10 (carboxylic acid) alone were determined and plotted, as shown in Fig. 1. The metal extraction pH isotherms using

the combination of 0.5 M Versatic 10 and 0.35 M LIX63 (hydroxyoxime) were also determined and plotted in Figure 2. Comparison of the two figures reveals that the combination of LIX63 with Versatic 10 resulted in significant synergistic extraction isotherm shifts (to lower pH) for nickel, cobalt, copper, zinc, and manganese and antagonistic shifts (to higher pH) for calcium and magnesium. As shown in Figure 2, with the 0.5 M Versatic 10 / 0.35 LIX63 system, the ΔpH_{50} values of nickel, cobalt, copper, zinc, manganese and Ca were found to be 2.8, 3.5, >2.0, 2.0, 1.2 and -0.5 pH units, respectively.

pH_{50} of metals from pH isotherms in Figs 1 and 2

Metal	pH_{50}		ΔpH_{50}
	0.5M Versatic 10	0.5M Versatic 10 + 0.35M LIX 63	
Ni	6.2	3.4	2.8
Co	6.3	2.8	3.5
Cu	4.1	<2.0	>2.0
Zn	5.7	3.7	2.0
Mn	6.5	5.3	1.2
Ca	7.0	7.5	-0.5

The $\Delta pH_{50(Mn-Ni)}$ value for the 0.5 M Versatic 10 / 0.35 M LIX63 system was found to be 1.9 pH units and the $\Delta pH_{50(Mn-Co)}$ value 2.5 pH units, indicating easy separation of nickel and cobalt from manganese, calcium and magnesium. The $\Delta pH_{50(Ca-Mn)}$ value for the 0.5 M Versatic 10 / 0.35 M LIX63 system was found to be 2.2 pH units, indicating easy separation of manganese from calcium and magnesium.

Example 2 - Extraction kinetics with Versatic 10 / LIX63 synergistic system.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Cu, Co, Zn and Mn display fast extraction kinetics, while the extraction kinetics for Ni are slow. Hence this system is potentially suitable for Cu, Co, Zn and Mn recovery when

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the leach solution contains little Ni.

Tests were conducted to establish the extraction kinetics of the metals in the synthetic laterite solution using Versatic 10/LIX63. The extraction kinetics of copper, cobalt, zinc (and manganese - see Example 6 and Fig 8) were found to be fast and the extraction kinetics of nickel were found to be relatively slow (Fig. 3). Within 30 seconds, only 55% Ni was extracted and within 2 minutes, only 74%. It is noted that Mn and Zn are crowded out as Ni extracts.

<u>Example 3</u> - Stripping kinetics with Versatic 10 / LIX63 synergistic system.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Cu, Co, Zn and Mn display fast stripping kinetics, while the stripping kinetics for Ni are slow. Hence this system is potentially suitable for Cu, Co, Zn and Mn recovery when the leach solution contains little Ni.

Tests were conducted to determine the stripping kinetics of the metals from the 0.5 M Versatic 10 / 0.35 M LIX63 system using a strip solution containing 5 g/L Ni and 10 g/L sulphuric acid (Fig. 4). The stripping kinetics of copper, cobalt and zinc were fast. The stripping kinetics of nickel were slow, with only 18% of the nickel being stripped after 2 minutes of mixing.

<u>Example 4</u> - Stripping of cobalt from LIX63 alone and Versatic 10 / LIX63 systems.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Co displays fast stripping kinetics, however when LIX 63 alone is used, Co cannot be readily stripped thus making LIX 63

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alone an unsuitable extractant for Co-containing solutions.

Cobalt(II) can poison hydroxyoxime reagents such as LIX63. This means that once cobalt(II) is extracted by hydroxyoxime reagents (and oxidises to Co(III)), it cannot be stripped with concentrated acids. Tests were conducted to see whether the new system results in cobalt poisoning of the extractant/synergist.

Parallel tests were conducted with 0.35 M LIX63 alone and 0.5 M Versatic 10 / 0.35 M LIX63 systems by mixing the organic solutions with aqueous solution containing cobalt (Fig. 5). The organic and aqueous solutions were left in contact with air bubbling for 76 hours. Thereafter, a sulphuric acid solution of 100 g/l sulphuric acid was used to strip cobalt from the loaded organic solution sample. The cobalt stripping efficiency from the 0.35 M LIX63 alone system was only 29.2% after 10 minutes stripping. The cobalt stripping efficiency for the 0.5 M Versatic 10 / 0.35 M LIX63 system was 99.5%. This indicates that cobalt(II) does not poison the Versatic 10 / LIX63 system.

<u>Example 5</u> - Extraction pH isotherms of metals with Versatic 10 / LIX63 system.

This example illustrates that when Versatic 10 is used as the extractant with no added synergist, the pH isotherm of Mn is too close to the isotherms of the "impurity elements" Ca and Mg for effective separation. However when the synergistic system comprising Versatic 10 and LIX 63 is used, the isotherm of Mn is sufficiently separated from the isotherms of Ca and Mg to allow effective separation.

The aqueous solution was a synthetic solution to simulate a typical waste laterite leach solution containing 1.46

g/L Mn, 17.6 g/L Mg and 0.54 g/L Ca.

The extraction pH isotherms were determined for 0.5 M Versatic 10 alone and 0.5 M Versatic 10 / 0.2 M LIX63 systems and shown in Figs. 6 and 7, respectively. The $pH_{50(Mn)}$ decreased from 6.9 to 5.6 pH units while the positions of isotherms of magnesium and calcium remained virtually unchanged. At pH 6.5, the extractions of manganese, calcium and magnesium were 17.9%, 2.84% (or 46 ppm) and 0.16% (or 82 ppm), respectively, for the Versatic 10 alone system while the extractions of manganese, calcium and magnesium were 87.3%, 2.41% (or 39 ppm) and 0.05% (or 26 ppm), respectively, for the Versatic / LIX63 system. This indicates that the selectivity of Versatic 10 for manganese over magnesium and calcium was very greatly improved.

Example 6 - Extraction kinetics with Versatic 10 / LIX63 system.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Mn displays fast extraction kinetics. Hence this system is suitable for Mn recovery.

The extraction kinetics of the metals in the synthetic waste laterite leach solution using the 0.5 M Versatic 10 / 0.2 M LIX63 system were determined and graphed in Fig. 8. As shown, the extraction kinetics of manganese were fast. Within 0.5 minutes, the system almost reached equilibrium with manganese extraction of 80%.

Example 7 - Stripping kinetics with Versatic 10 / LIX63 system.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Mn displays

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fast stripping kinetics. Hence this system is suitable for Mn recovery.

The stripping kinetics of the manganese in the loaded 0.5 M Versatic 10 / 0.2 M LIX63 system were determined using a strip solution containing 60 g/L Mn and 35 g/L sulphuric acid and graphed in Fig. 9. As shown, the stripping kinetics of manganese were fast. Within 0.5 minutes, the system almost reached equilibrium with manganese extraction of 99%.

Process Flowcharts

Example 8 - Process for separation and recovery of cobalt and manganese from leach solutions.

Based on the above findings, a new direct solvent extraction (DSX) process flow sheet was designed. The flow sheet is shown in Figure 10.

Leach solution

The leach solution contains manganese and cobalt, as well as the impurity elements calcium and magnesium, but little or no copper, zinc or nickel. A suitable solution composition for this flow sheet may comprise Co > 200 ppm, Mn > 1 g/L, Ca < 50 g/L (Ca will be < 1 g/L in sulphate solutions), Mg < 100 g/L, Cu, Zn and Ni < 100 ppm (or of no economic value). It is noted that the flow sheet is not limited to such leach solutions, and the leach solutions may comprise different levels of the given elements, optionally together with further impurity elements. This leach solution is one that may have been subjected to preliminary neutralisation with limestone at pH 4.5 - 5.0 to precipitate impurity elements Fe (III), Al, Si and Cr.

Synergist solvent extraction (SSX EX)

In the synergistic solvent extraction step, an organic solution of carboxylic acid (Versatic 10), a hydroxyoxime (LIX 63) and a stabilizer (Ionol) in organic diluent Shellsol 2046 is contacted with the leach solution at pH 6 - 6.5 to obtain (a) an aqueous raffinate containing magnesium and calcium, and (b) a loaded organic solution containing almost all of the cobalt and manganese, and only minor levels of calcium and magnesium.

Scrubbing (SC)

The organic solution from the extraction step is subjected to scrubbing at pH 5.5 - 6 using a sulphate solution containing a small amount of manganese from the next step of stripping 1, resulting in (a) a scrubbed organic solution containing cobalt and manganese, and (b) a scrub liquor which is recycled to the synergistic solvent extraction step.

Selective stripping (ST1)

The scrubbed organic solution is subjected to stripping 1 (selective strip) using a sulphuric acid solution at pH between 4.0 - 5.0 resulting in (a) a loaded strip liquor containing manganese, and (b) a stripped organic solution containing mainly cobalt and only a very small amount of manganese.

The loaded strip liquor is sent to manganese recovery, with one stream returning to the previous scrubbing stage.

Scrubbing (SC2)

The organic solution from stripping 1 is subjected to scrubbing 2 at a pH of 3.5 - 4.0 using the aqueous strip liquor from a subsequent stripping stage (stripping 2). This step results in (a) a scrubbed organic solution containing cobalt, and (b) a scrub liquor which is recycled to the original synergistic solvent extraction stage to maximize cobalt recovery.

Stripping (ST2)

The scrubbed organic solution is subjected to stripping 2 using sulphuric acid solution at pH between 2.0 - 2.5. The cobalt recovered in this stripping stage is optionally subjected to zinc/copper/nickel ion exchange to enable removal of any zinc, copper and nickel impurities present. The zinc, copper and nickel is disposed of, and the cobalt is sent to cobalt recovery by any process known in the art. One example is cobalt precipitation using base or sulphide.

Example 9 - Process for separation and recovery of cobalt from leach solutions.

An alternative solvent extraction process flow sheet was formulated for the recovery of cobalt from leach solutions containing impurity elements manganese, calcium and magnesium, with little or no copper, zinc or nickel. This flow sheet is shown in Figure 11. A typical solution composition for which this flow sheet could be applicable comprises Co > 200 ppm, Mn < 100 g/L, Ca < 100 g/L (Ca will be < 1 g/L in sulphate solutions), Mg < 100 g/L, Cu, Zn and Ni < 100 ppm (or of no economic value). Of course, variations in this solution composition are possible.

The plant leach solution (PLS) is adjusted to a pH between 4.0 - 5.0 and subjected to the synergistic solvent extraction (SSX) described in relation to Example 8 above. The organic phase contains the cobalt (as well as zinc, copper and nickel to the extent that these are present) and a minor level of manganese. The aqueous raffinate contains magnesium, calcium and manganese.

Scrubbing is conducted as described above in relation to Example 8, at pH 3.5 - 4.5, yielding (a) a scrubbed organic solution containing principally cobalt, but also

zinc, copper, and nickel in very low quantities if present at all in the plant leach solution, and (b) a scrub liquor which is recycled to the original synergistic solvent extraction stage to maximize cobalt recovery.

The organic phase of the scrubbing step contains cobalt, and possibly zinc, nickel and copper, which is then subjected to stripping with sulphuric acid at pH between 2.0 and 2.5. The loaded strip liquor is sent to cobalt recovery (with one stream returning to the previous scrubbing stage), optionally via ion exchange, with the organic phase returned to the synergistic solvent extraction.

Example 10 - Process for Separation and Recovery of Cobalt, Copper and Zinc.

Figure 12 details a process flow sheet which is a variation on that illustrated in Figure 11, and described in Example 9 above.

The process of Figure 12 is suitable for recovering copper, cobalt and zinc from leach solutions that contain impurity elements manganese, calcium and magnesium, with little or no nickel. A solution composition to which this process may suitably be applied contains the following: Cu > 500 ppm, Co > 200 ppm, Zn > 500 ppm, Mn < 100 g/L, Ca < 100 g/L (Ca will be < 1 g/L in sulphate solutions), Mg < 100 g/L and Ni < 100 ppm (or of no economic value). Of course, variations in this solution composition are also envisaged.

The plant leach solution is subjected to copper solvent extraction and copper electrowinning. The leach solution containing reduced levels of copper, and all other elements, is then subjected to iron and aluminium precipitation (Fe/Al PPT) by neutralising the leach solution with limestone to a pH of between 4.0 - 5.0 to

precipitate iron and aluminium. The leach solution is then subjected to the synergistic solvent extraction, scrubbing and stripping as described in relation to Example 9 and Figure 11 above. As will be appreciated, any copper and zinc still present reports to the phases to which the cobalt reports.

The aqueous phases collected from scrubbing and stripping contain cobalt, zinc and minor levels of copper, together with any levels of nickel which may be present. The aqueous liquor is subjected to zinc solvent extraction to remove zinc therefrom for recovery. Thereafter, the cobalt (and nickel and copper) containing solution is subjected to nickel and copper ion exchange to enable nickel and copper removal and disposal. Thereafter, the cobalt is recovered.

Example 11 - Process for separation and recovery of manganese from leach solutions.

A new solvent extraction process flow sheet was developed for recovering manganese from leach solutions that contain the impurity elements calcium and magnesium, with little or no copper, zinc, cobalt or nickel. This is set out in Figure 13. A typical solution composition which may be subjected to this process may comprise Mn > 1 g/L; Ca < 50 g/L (Ca will be < 1 g/L in sulphate solutions); Mg < 100 g/L; Cu, Zn, Co and Ni < 100 ppm (or of no economic value). Of course, variations in this solution composition are envisaged.

The leach solution, which may have been subjected to preliminary processing steps, is subjected to synergistic solvent extraction with the Versatic 10 / LIX 63 / Ionol synergistic system, with the aqueous phase adjusted to a pH between 6.0 - 7.0. The aqueous raffinate contains calcium and magnesium, and the organic phase contains

manganese, with minor levels of calcium of magnesium. The organic phase is subjected to scrubbing using a scrub solution at pH between 6.0 - 6.5. The scrub solution is a stream of the manganese sulphate solution generated in a subsequent stripping stage. The organic phase from the scrubbing stage containing manganese is sent to stripping, and the aqueous scrub liquor is recycled to the synergistic solvent extraction stage.

Stripping is performed on the organic phase using sulphuric acid at pH between 3.0 - 4.0. The aqueous strip liquor is optionally subjected to sulphide precipitation to remove any copper, zinc, cobalt or nickel impurities present, and the manganese sent to manganese recovery. A stream of the strip liquor is recycled to the scrubbing stage. This process is particularly suited for situations where the manganese value is acceptable, making it desirable to recover the manganese from a leach solution. If the leach solution contains appreciable levels of cobalt, and other elements having pH isotherms similar to cobalt, then the process of Example 8 and Figures 10 would be more suited.

Example 12 - Effect of stabilizer (Ionol) on degradation of hydroxyoxime (LIX63) in Versatic 10 / LIX63 system.

This example shows how addition of an anti-oxidant stabilizer (Ionol) slows the rate of degradation of the hydroxyoxime LIX63 in the Versatic 10 / LIX63 extraction system.

An organic extractant solution (25 mL) containing 0.4M LIX63 and 0.5M Versatic 10 in Shellsol D70 diluant was loaded with a synthetic leach solution (50 mL) containing 0.5 g/L Ca, 9 g/L Na, 24 g/l Mg, 45 g/L Mn, 0.2 g/L Co, 1 g/L Zn and 0.15 g/L Cu, at pH 4.5 and left to stand in a water bath at 25°C. Two further (duplicate) systems, each

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containing 10 g/L Ionol were prepared and treated similarly. After 18 days, the organic solution was sampled and analysed for LIX63 using gas chromatography. The results are shown in the table below. After 18 days in the Ionol-free system, 5.2 % of the LIX63 had been degraded. After 18 days in the duplicate systems initially containing 10 g/L Ionol, 0.7% and 1.6% of the LIX63 had been degraded.

Table 1 Oxime concentration in the loaded organic solutions as a function of contact time.

	LIX63 (%) relative to initial concentration		
Contact time (days)	Versatic 10 + LIX63	Versatic 10 + LIX63 + Ionol	Versatic 10 + LIX63 + Ionol
0	100.0	100.0	100.0
8	97.0	99.6	99.2
18	94.8	99.3	98.4

It will be understood to persons skilled in the art of the invention that many modifications may be made to the embodiments described without departing from the spirit and scope of the invention.

Dated this 29th day of October 2004

<u>COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION</u>

By their Patent Attorneys

GRIFFITH HACK

Fellows Institute of Patent and Trade Mark Attorneys of Australia

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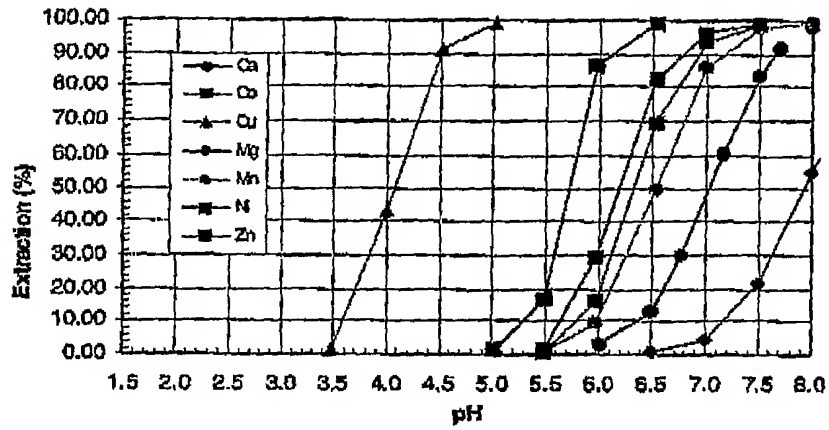

Figure 1

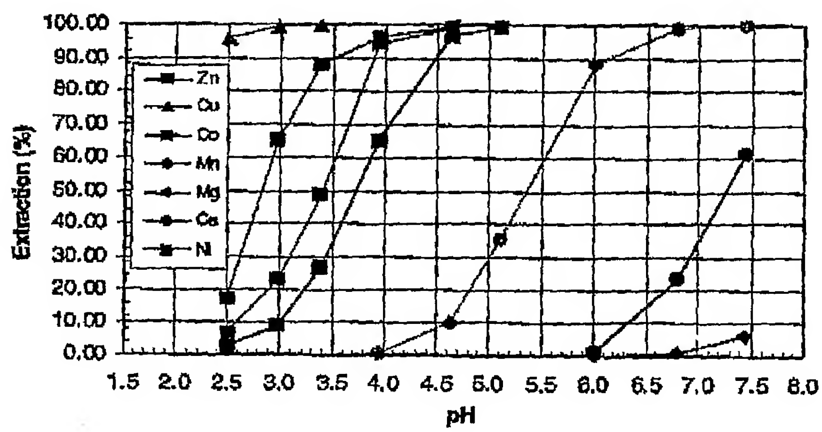

Figure 2

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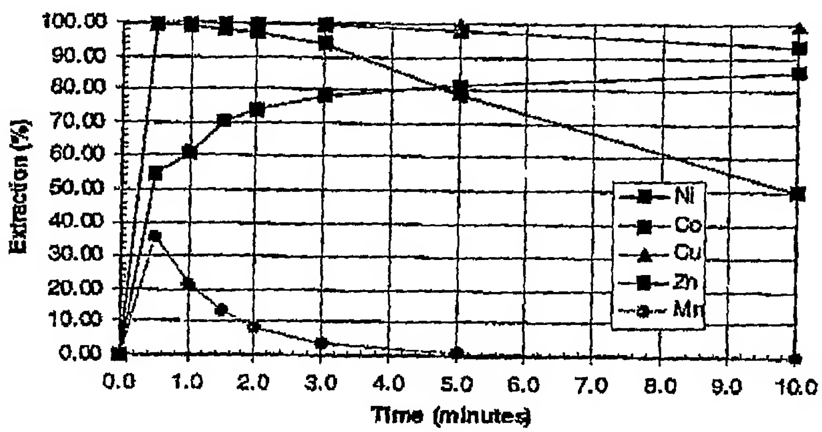

Figure 3

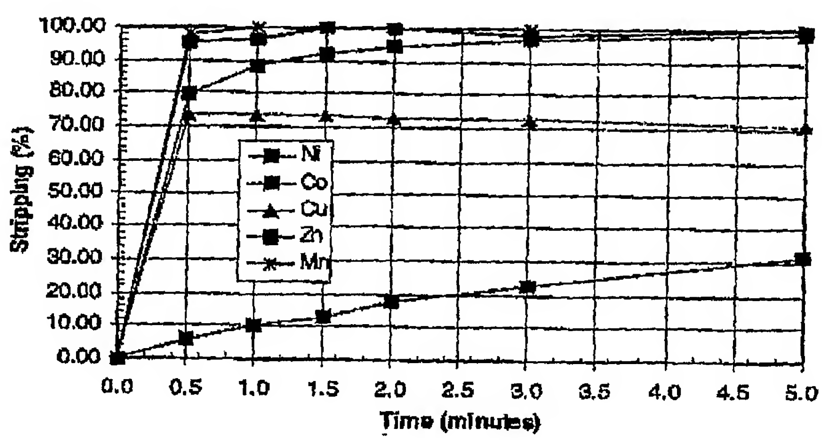

Figure 4

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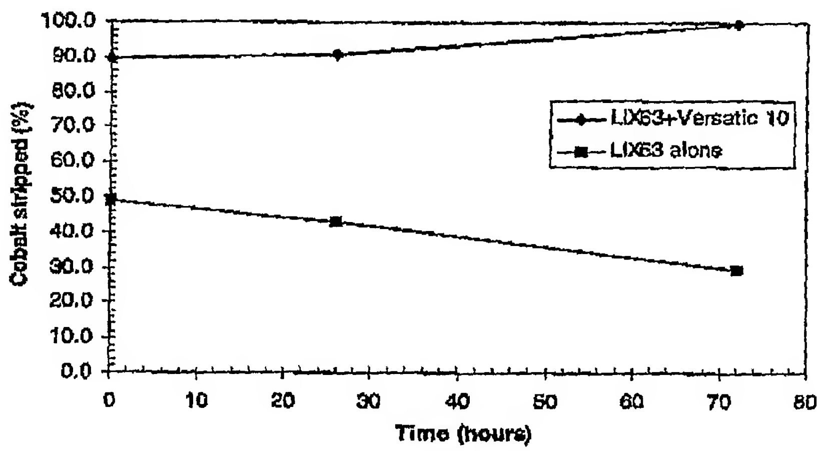

Figure 5

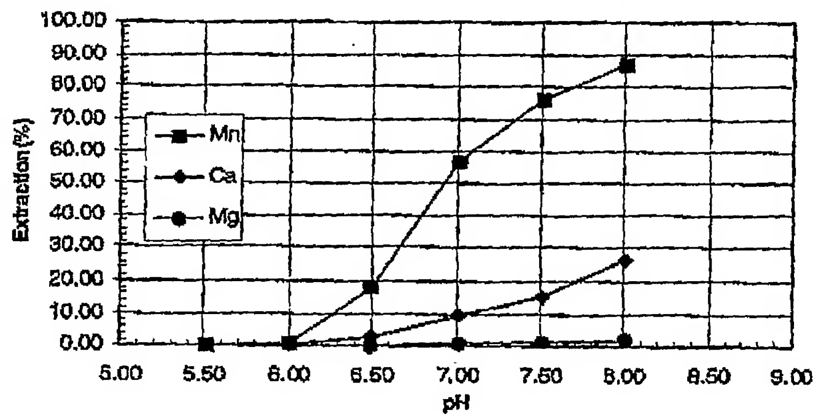

Figure 6

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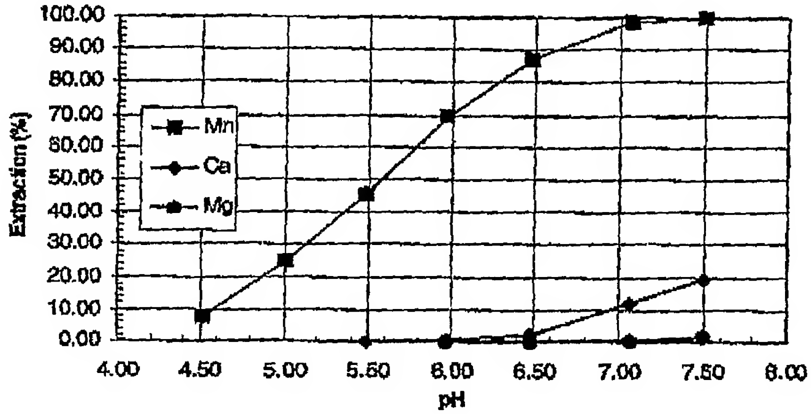

Figure 7

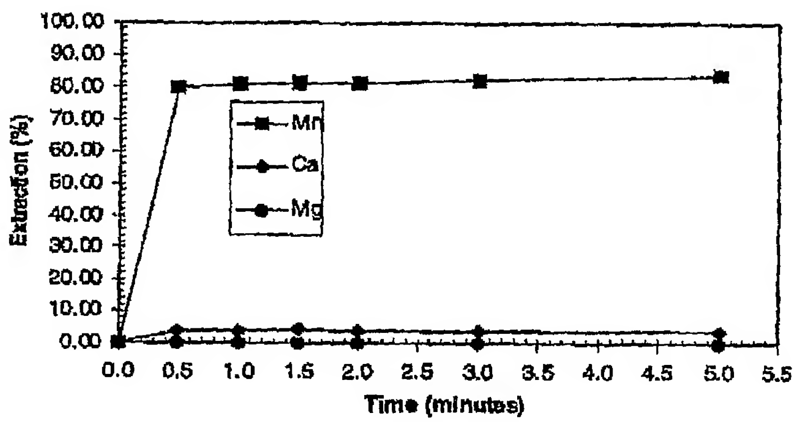

Figure 8

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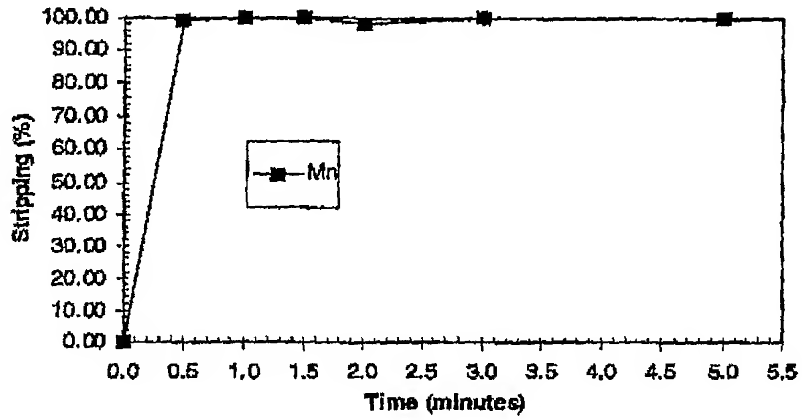

Figure 9

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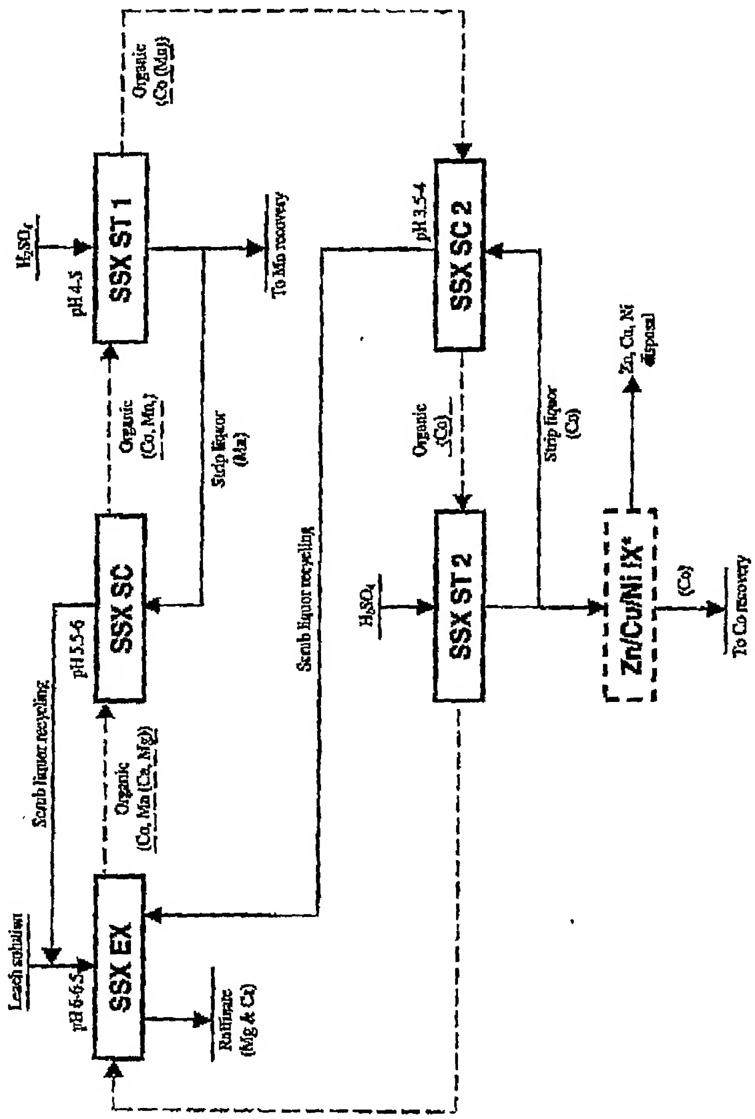

Figure 10

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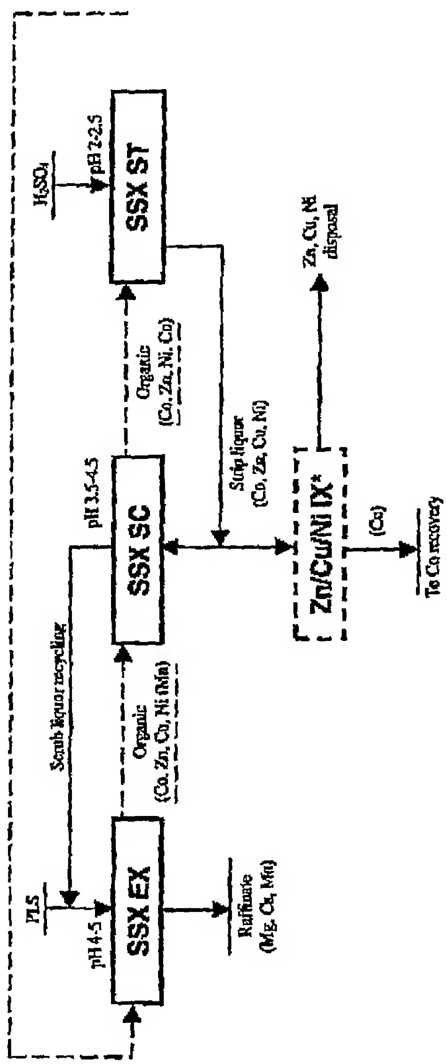

Figure 11

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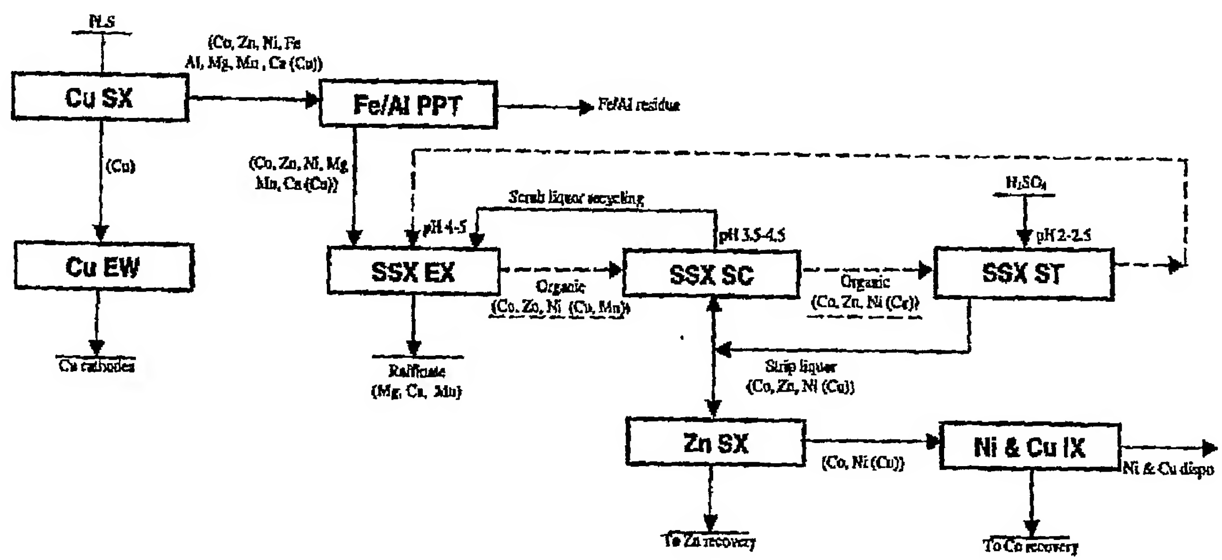

Figure 12

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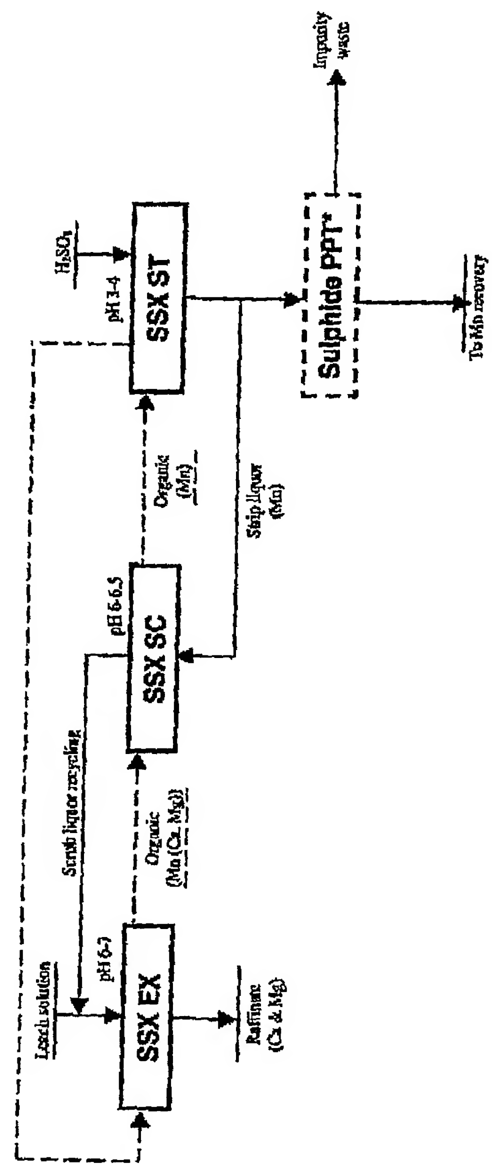

Figure 13